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**(54) Method and apparatus for performing growth of thin films of a compound.**

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(73) Proprietor: Oy Lohja AB  
Ahertajantie 3  
SF-02100 Espoo 10 (FI)

(72) Inventor: Suntola, Tuomo  
Jalkajousentie 15  
02610 Espoo 61 (FI)  
Inventor: Pakkala, Arto  
Joupinkuja 4  
02760 Espoo 76 (FI)  
Inventor: Lindfors, Sven  
Nuottamiehentie 8  
02230 Espoo 23 (FI)

(74) Representative: Tiedtke, Harro, Dipl.-Ing.  
Patentanwaltsbüro Tiedtke-Bühling-Kinne-  
Gruppe-Pellmann-Grams-Struif Bavariaring 4  
Postfach 20 24 03  
D-8000 München 2 (DE)

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## Description

### Background of the invention

The present invention provides a useful tool for performing the method for producing thin films of a compound presented in U.S. Pat. No. 4,058,430. According to that method, referred to as ALE (Atomic Layer Epitaxy), high quality thin films of a compound can be produced by subjecting the surface to be grown to successive reactive vapours which make the surface grow by a single atomic layer in each reaction step.

When compared to thin film deposition concepts of the prior art, the ALE demand for separated surface reactions of different reactive vapours gives rise to special requirements for the equipment and method for performing the ALE growth. In U.S. Pat. No. 4,058,430 these requirements were approached using classical vacuum deposition techniques by providing separate reaction regions or periods, separated from each other by a region or period of high vacuum condition. Due to leaks of the reactive vapours from the reaction regions, and due to residual vapours especially in the case of exchange surface reactions, difficulties are found in obtaining the high vacuum condition needed for the successful separation of the reaction steps. These problems take away from an advantage of the ALE-method, wherein the self-stabilizing growth rate property of the ALE-method is obtained by using quantities of reactive atoms in excess to the amount needed for a full surface coverage in a single surface reaction step.

### Summary of the invention

Object of this invention is to provide a method and apparatus for producing a thin film of a compound of different elements on a substrate by an atomic layer epitaxy growth which overcome the above described difficulties which arise from using vacuum deposition techniques in performing the ALE growth method. An essential feature of the present inventions is the use of gas phase diffusion barriers in order to separate the single surface reactions steps. According to the present invention the diffusion barrier techniques are also used to perform valve actions to control the flow of reactive vapours from their sources to the surface reaction zone, and to separate the exhaust condensation zone from the reaction zone. Furthermore, the gas phase medium used in the formation of the diffusion barriers can be used as a carrier gas to transfer the reactive vapours from their sources to the surface reaction zone and to transfer the residual vapours from the surface reaction zone to the exhaust.

The use of inert gases as carrier gases or as protective gases is known in the prior art in several connections, as for example, in the field of gas chromatography, and in Chemical Vapour Deposition (CVD) methods which are widely used in the semiconductor industry. In general, it may be helpful to regard the present invention as shifting the performance of ALE-growth from a

Molecular Beam Epitaxy-MBE-type process towards the techniques of CVD. One practical advantage of the known CVD-method over the vacuum deposition methods is that the growing of the thin films may be carried out in an inert gas instead of in high vacuum, which usually brings about more economic and more productive apparatus solutions. Correspondingly, this advantage is also achieved by the method and apparatus according to this invention. Additionally, the advantages over the CVD-method achievable by applying the ALE-method and apparatus according to this invention to the growing of thin films according to the CVD-method are comparable to the substantial advantages over the classical vacuum deposition methods including the MBE-method achievable by applying the method and apparatus according to US Patent No. 4058430 to the growing of thin films according to the vacuum deposition methods including the MBE-method.

It is stressed that the present invention is not only an alternative to the method disclosed in US Pat No 4058430 for performing ALE growth, but it also gives rise to new advantages as compared to the prior art in general relating to thin film growth of a compound. These advantages include the ease with which exchange surface reactions can be effected, wherein the elemental components of the compound to be grown are allowed to be brought to the surface reaction area in the form of a second compound of the element in question. This is of particular interest when dealing with metals having low vapour pressures, which thus can be replaced by more volatile compounds such as metal halides or organometals. Accordingly, a decreased source temperature is permitted, as well as a decrease in the substrate temperature needed for a perfect back-evaporation after the formation of a full surface coverage according to the ALE-principle. Concerning the growth of metal oxides, according to present knowledge, a metal halide is chemisorbed onto an oxygen surface in halide molecule form, until the halogen atoms are released in the next surface reaction step by hydrogen atoms from water molecules used as the reactive vapour in the oxidizing surface reaction step.

Another advantage of the exchange reaction can be obtained in the growth rate properties. For example, in the case of direct elemental surface reactions, as in the case of a ZnS growth, the monoatomic metal surface layer has a tendency to re-evaporate before the surface reaction with sulphur vapour. Thus the growth rate is dependent on the re-evaporation time between Zn- and S-surface reaction steps; and, further, it decreases with increasing temperature. In the case of corresponding exchange reactions this drawback does not take place and a constant growth rate of substantially 0.1 nm/cycle is observed in a wide range of temperatures and re-evaporation times. It has been observed that each compound has its own typical growth rate corresponding to a stable monolayer

configuration according to the crystal structure properties in question.

The apparatus according to the present invention is mechanically simpler than that according to the prior art. Important advantages have also been obtained in the operation and maintenance characteristics of such apparatus of present invention. The apparatus is suitable for large area production, due to the effective utilization of the self-stabilizing growth rate property of the ALE process.

The method of the present invention sets certain prerequisites as to the shape of the substrates to be used, due to the necessity of maintaining certain "aerodynamics" in order to obtain fast operation. Ideal substrates are flat plates with smooth surfaces such as glass plates, etc. The operational properties of the ALE-method provides a possibility for tailored layer structures and doping, and such products are easily obtained with the method of the present invention. Reactive vapour in a single surface reaction step may contain several components, which are able to react with the surface to be grown, but it must not contain such components which react with each other resulting in any solid state compound at the temperature of the surface to be grown. For example, a basic ZnS growth can be modified by adding a small amount of  $\text{MnCl}_2$  vapour to the  $\text{ZnCl}_2$  reaction steps.  $\text{MnCl}_2$  and  $\text{ZnCl}_2$  do not react with each other, but each of them reacts with the solid sulphur surface resulting in Mn doped ZnS. Mixed compounds can be made in the same way, i.e. by adding  $\text{CdCl}_2$  vapour to the  $\text{ZnCl}_2$  reaction step in a ZnS growth thus resulting in a  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  film. Corresponding doping or mixing is possible with the VI group or any other group elements. A condition for obtaining the ALE-type growth according to the method of the present invention is that simultaneous interactions of such vapours, which are able to react with each other at the temperature of the substrate surface resulting in solid state reaction products at the said temperature, are prevented with the aid of diffusion barriers formed by a gas phase medium such as in form of a carrier gas. The gas phase medium should be principally inert with respect to the growing surface. Some secondary influences may be, however, included, such as addition of doping agents, catalytic or inhibitory actions and chemical transport of surface reaction residues.

#### Brief description of the drawings

Preferred embodiments of the invention will be described in conjunction with the accompanying drawings, in which:

Fig. 1 illustrates pulses of reactive vapours AX and BY and the diffusion barrier V between such pulses;

Fig. 2 is a schematic sectional view of an embodiment for carrying out the method of the invention;

Fig. 3 is a transverse section of the structure of Fig. 2 taken along line III—III;

Fig. 4 illustrates the self-stabilizing growth rate effect obtained with the method of the present invention as compared to the prior art;

Fig. 5 shows a typical magnetic valve used to produce a reactive vapour pulse source in accordance of the method of the present invention;

Fig. 6 is a schematic illustration of an embodiment of a source of reactive vapour pulses according to the method of the present invention;

Fig. 7 is a simplified flow circuit constituting an analog of the source embodiment of Fig. 6;

Fig. 8 is a schematic vertical section view of another embodiment of apparatus used to carry out the method of the present invention;

Figs. 9A—9C are transverse sectional views of Fig. 8, taken along line IXA—IXA, IXB—IXB, and IXC—IXC, respectively;

Fig. 10 is a schematic vertical sectional view of an embodiment which is principally compatible with that of Fig. 1;

Fig. 11 is a sectional top view of the embodiment of Fig. 10;

Fig. 12 is a sectional view of the embodiment of the source of Fig. 6 used in the embodiment of Fig. 10;

Fig. 13 is a schematic illustration of another embodiment of apparatus used to carry out the method of the present invention, and is a vertical sectional view taken along line XIII—XIII of Fig. 14;

Fig. 14 is a schematic horizontal sectional view of the embodiment of Fig. 13 taken along line XIV—XIV;

Fig. 15 is a schematic illustration of an electroluminescence (EL) thin film structure produced with the aid of the present invention according to example 4;

Fig. 16 illustrates measured brightness and efficiency curves for the EL-structure of Fig. 15; and

Fig. 17 shows measured electrical properties of an  $\text{Al}_2\text{O}_3$  thin film prepared according to example 5.

#### Detailed description of the preferred embodiments

In accordance with the present invention pulses of different vapours of substances (hereafter referred to as reactive vapours) are successively applied to a substrate to cause growth of a thin film of a compound. For example, as depicted in Fig. 1, such pulses of reactive vapours AX and BY at partial pressures  $P_0$ , having a diffusion barrier V therebetween, are conducted through the reaction chamber, wherein the length of the diffusion barrier is  $X_B$  in the gas phase medium G having a velocity  $v$  in the X direction. The quantity  $t_B$  represents the time duration of the diffusion barrier, which substantially prevents interaction of the vapour of substances, thus precluding any appreciable effect therefrom on the final product.

The embodiment shown in Figs. 2 and 3

comprises a glass tube as the main body of the structure, vapour source means 20 with connections 12 to the reaction zone 18 in the main body tube, a vacuum pump 17 with an exhaust connection 13 from the main body tube for maintaining a pressure  $P_r$ , and a heater 15 surrounding the reaction zone 18. A substrate or substrates 11 are placed in the reaction zone through the opening 14 at the end of the body tube 10. During the growth of the thin films 100 on the substrates, the substrate temperature is maintained with the aid of heating elements 16 controlled by standard regulator means. Reactive vapour pulses from the vapour source means 20 are controlled by a standard timing unit and directed sequentially to the reaction zone according to the ALE-principle and the method of the present invention.

As referred to herein, the present invention provides a self-stabilizing growth rate effect, and a comparison thereof with the prior art is shown in Fig. 4. Curve *a* illustrates the thickness profile of a thin film grown in accordance with the principles of the present invention, and utilizing the apparatus of Figs. 2 and 3. On the other hand, a thickness profile *b* results from the growth of a corresponding thin film effected by means of the prior art where two reactive vapours are caused to react simultaneously with the substrate.

Two principal techniques have been used to actuate the pulses of the reactive vapours. One is the use of mechanical valves, constituting a straightforward technique for reactive materials which are effectively volatile at room temperature. This kind of solution is represented in Fig. 5 where reference numeral 25 indicates the connection tube to the reactive vapour source, reference numeral 21 depicts a valve body having a valve solenoid 22 and a lock element 23, and where the valve opening 26 and a connection to gas phase medium supply 28 communicate directly with the source connection tube 12. A gas phase medium in form of a carrier gas flow is useful to minimize tail formation to reactive vapour pulses in the source connection tube 12. The valve action is controlled by a timing unit 30.

The other approach to the pulse source embodiment is schematically presented in Fig. 6. In this approach the mechanical valve action is replaced by controllable diffusion barriers in the connection tube between the vapour source and the reaction chamber. This type of vapour source is preferable in cases where the reactive substance has a low vapour pressure and must therefore be conducted to the reaction chamber at an elevated temperature. The reactive vapour is produced by heating a reactive substance *M* in solid or liquid form in a source region 41 with the aid of a heating element 47. In a lock condition a diffusion barrier is formed in a source opening tube 43 with the aid of the gas phase medium supplied from a connection tube 49 and exhausted through a connection tube 46 to a suction pump 50. A corresponding diffusion barrier is formed in the source connection tube 12

in order to prevent the vapours in the reaction chamber from diffusing to the source. The conditions needed for such diffusion barriers are described in detail hereinbelow.

In the lock condition the reactive vapour produced in the evaporation region 41 is transferred to a condensation region 42, which can be cooled with the aid of a cooling element 48. The lock condition of the vapour source is changed to a feeding condition by controlling a valve 44 to admit a gas phase medium in form of an extra carrier gas flow, which is high enough to turn the flow direction in the source opening tube 43. The vapour source operation is described in detail with the aid of the flow circuit analogy presented in Fig. 7.

An embodiment which may be used to demonstrate the method of the present invention by means of the various examples given herein, is illustrated in Figs. 10 and 11. For its working principle it is identical to the embodiment of Figs. 2 and 3 and contains a tube-like reaction chamber 18 plus vapour source and exhaust means. The body of the reaction chamber 110 is made of stainless steel which is covered with inner glass plates 96. The exhaust means includes a heating element 116, a condensation region 19, and a gas flow steering wall 115. Temperature regulators and a source pulse timing unit are illustrated respectively by the blocks 90 and 91. Fig. 12 shows the vapour source means applied to the embodiment of Figs. 10 and 11 in accordance with the principles presented in Figs. 6 and 7. In this structure the tubes 12, 49 and 43 have been constructed with the aid of a coaxial glass tube array formed by vapour source opening 43 and a glass tube 84. The outer body 86 of the source means is of stainless steel.

A common feature of the embodiments in Figs. 2 and 3 and Figs. 10 and 11, is that the substrates are in a fixed place in the reaction chamber during the thin film growth. The reactive vapour pulses pass through the chamber and are driven by a gas phase medium which forms diffusion barriers between the pulses of the reactive vapours.

Another approach to the method of the present invention comprises the use of embodiments having locally fixed streams of the reactive vapours, separated from each other by locally fixed streams of said gas phase medium forming the diffusion barriers. In such embodiments the cyclic alternative interactions between the substrate surface and each reactive vapour stream in turn is made by rotation or other periodic mechanical movement of the substrates. From the point of view of the substrate surface the situation is quite similar in both cases, wherein the substrate is successively subjected to the interaction of each reactive vapour in a gas phase medium which keeps said reactive vapours separated by building diffusion barriers between them. Embodiments with locally fixed streams of the reactive vapours are presented in Figs. 8, 9A, 9B, 9C and Figs. 13, 14. In the embodiment of Figs. 8, 9A, 9B and 9C two reactive vapour sources 53

and 54 are placed in opposite columns 51 and 52 of the body 60 of the apparatus. The sources are heated with heaters 56. The reactive vapours flow up by diffusion or with the aid of said gas phase medium and meet the substrates 11', which are placed in a rotating holder 61 forming a structure resembling a paddle wheel. When the paddle wheel is rotating, the substrates will meet each reacting vapour stream in turn when passing the columns 51 and 52, respectively. Streams of said gas phase medium from tubes 66 and 67 in columns 55 sweep up the reactive vapours between the substrates while they are passing the columns 55. The flow passages for said inert gas phase medium are connected by one end to a suction pump and by the other end to said source of said gas phase medium. The flow passages for the different vapours of said substances are connected by one end to a suction pump and by the other end to said vapour sources. In the channels between the substrates the flow conditions are nearly identical with those in the embodiment of Figs. 10 and 11. In Fig. 8, reference numeral 64 indicates the means for substrate rotation, while a heater 68 is provided at the reaction zone, and walls 57 are provided between the vertical flow columns. In Fig. 9A, reference numbers 51', 52', 55' and 57' correspond to reference numbers 51, 52, 55 and 57 in Fig. 9C, respectively.

In the embodiments of Figs. 13 and 14 the sequential interactions between the substrate surface and the reactive vapours of said substances are made by a reciprocating motion of the substrate 11' over a fixed array of source openings 75, carrier openings 73 and exhausts 74. Diffusion barriers E are formed between the substrate surface and the gas flow array body 72. In accordance with calculations as set forth below, operation with this embodiment is possible even at atmospheric pressure without an unpractically high total flow rate of the gas phase medium. In Figs. 13 and 14, element 77 is the gas phase medium feed tube, 79 the vapour source connections, 78 the exhaust and 81, 82 the reactive vapour sources.

Because an ALE-type process generally consists of thousands of single surface reaction steps in a thin film growth, the total process time  $t_p$  tends to become long unless special attention is paid to minimize the contributing delays in the reaction cycles. Generally a figure of merit E of a thin film process can be given by the formula

$$E = T \cdot A_s / (t_p + t_L), \quad (1)$$

where T is the film thickness,  $A_s$  the substrate area to be covered,  $t_p$  the process time and  $t_L$  the time for loading and unloading the apparatus. The apparatus cost, power consumption and source material efficiency are not considered in this comparison.

In an ALE-type process the thickness of the thin film can be expressed in form

$$T = N \cdot T_o, \quad (2)$$

where  $T_o$  is the thickness obtained in one reaction cycle and N the number of cycles. The process time,  $t_p$ , can be expressed by

$$t_p = N \cdot t_o, \quad (3)$$

where the time of one cycle,  $t_o$ , is the sum of pulse times of different reactive vapours  $t_1, t_2, \dots, t_m$  and the time intervals  $t_{11}, t_{12}, \dots, t_{1m}$  between them needed to build up the diffusion barriers. In the case of a simple binary compound AB,  $t_o$  has the form

$$t_o = t_A + T_{1A} + t_B + t_{1B}. \quad (4)$$

The substrate area  $A_s$  handled in a process is mainly determined by the equipment size and can be varied in wide limits within the embodiments of this invention. The operational analysis, which also includes the effect of the size of the apparatus, is practically made by analyzing the time contributions  $t_m$  and  $t_{1m}$  in a reaction cycle. A detailed analysis is made for the case of the embodiments in Figs. 2, 3, 10, 11, where there is a carrier gas flow at a velocity v in a tube-like reaction chamber, with a free sectional area A according to Fig. 1, where the total pressure p, and a partial pressure  $p_o$  of the reactive vapour pulses AX and BY are propagated with the gas phase medium flow in the x-direction.

The reactive vapour pulses tend to broaden during the propagation due to diffusion in the carrier gas according to equation

$$\frac{\delta p}{\delta t} = D \Delta^2 p \quad (5)$$

where D is the diffusion constant of the reactive vapour in the gas phase medium. In laminar flow conditions in the reaction tube, and neglecting the effects of radial velocity profiles, equation (5) can be replaced by a one-dimensional diffusion equation in the x-direction

$$\frac{\delta p}{\delta t} = D \frac{d^2 p}{dx^2} \quad (6)$$

For simplicity the pressure  $P_o$  at the pulse edges is assumed to be constant during the diffusion which results in a boundary condition, and this assumption is also valid for consideration of the diffusion barrier in locally fixed cases such as in the source means of Figs. 6 and 7 and in the embodiment of Figs. 13 and 14. The solution of (6) is thus

$$p(x, t) = p_o \operatorname{erfc}(x / 2\sqrt{Dt}), \quad (7)$$

where x expresses the distance from pulse edges, and t is the time from pulse injection. An isobar of pressure p1 propagates from the pulse edges according to

$$x=2 C_1 \sqrt{Dt} \quad (8)$$

wherein  $C_1$  means

$$\operatorname{erfc} C_1 = p_1/p_0 \quad (9)$$

A diffusion barrier  $V$ , which is able to decrease the partial pressures of AX and BY to a value  $P_1$ , has a length  $X_B$  according to equation (8) and Fig. 1

$$X_B = 2 \cdot X_{p1} = 4 \cdot C_1 \sqrt{Dt} \quad (10)$$

At a gas phase medium velocity  $v$  the length of the diffusion barrier  $X_B$  at a distance  $L$  from the injection point of the reactive vapour pulses can be expressed in the form

$$X_B = 4 \cdot C_1 \sqrt{DLV} \quad (11)$$

which corresponds to the interval between the reactive pulses  $t_B$  as

$$t_B = X_B/v = 4 C_1 \sqrt{DLV}^3 \quad (12)$$

For practical expressions it is useful to give the diffusion constant  $D$  in form

$$D = D^*/p \quad (13)$$

where the constant  $D^*$  is independent of the pressure of the diffusion medium. Thus  $t_B$  can be given in form

$$t_B = 4 C_1 \sqrt{D^*} \sqrt{LV^3 p} \quad (14)$$

According to (14)  $t_B$  is strongly dependent on the gas phase medium velocity  $v$ , which can also be expressed in the form

$$v = S/A \quad (15)$$

where  $S$  is the pumping speed and  $A$  is the free sectional area of the reaction tube. A minimum carrier gas quantity for a certain value of  $t_B$  leads to high quantity at a low pressure, which cannot, however, go below  $p_0$ .

The pressure limits for the partial pressure of the reactive vapours,  $P_0$ , can be derived from the total atom or molecule dose needed for a full coverage of the substrate surfaces. According to the kinetic gas theory and the propagation geometry in question, the number of reactive gas molecules in a pulse can be expressed in the form

$$n_2 = v \cdot t_1 \cdot p_0 \cdot A/kT \quad (16)$$

where  $t_1$  is the duration of the reactive pulse. If the number of atoms needed to form a full surface coverage on a surface area unit is  $N_s$ , and the efficiency of the reactive vapour utilization is  $\eta$ , the number of molecules needed in a reactive vapour pulse is given by

$$n_1 = N_s \cdot A_s/\eta \quad (17)$$

where  $A_s$  is the substrate area. By making  $n_1 = n_2$  we have

$$P_0 = \frac{N_s \cdot A_s \cdot kT}{v \cdot t_1 \cdot A \cdot \eta} \quad (18)$$

Equation (18) gives, on the other hand, the pulse duration  $t_1$  for a given  $p_0$ . It can be found that for minimum  $t_1$  the value of  $p_0$  is increased. An upper limit to  $p_0$  is set by the pressure of the gas phase medium which was found to be advantageous for a minimized optimal flow level,  $p$ ,  $v$ , and  $t_0$  conditions. A low flow level is still useful for minimum radial profiles of the reactive vapour pressure  $p_0$ . For a simple binary compound AB growth from reactive vapours AX and BY, the minimum time of a process period  $t_p$  is

$$t_p = 2 (t_0 + t_1) \quad (19)$$

by making  $t_A = t_B = t_1$  and  $t_{1A} = t_{1B} = t_0$ .

In the embodiments of the present invention practical orders of magnitudes for  $t_0$  and  $t_1$  are 0.1 ... 1 and 0.05 ... 0.5 s, respectively, at a total pressure  $p$ , 0.5 ... 5 mb. As a subsequent check for the one dimensional diffusion analysis we can note that, typically, both the pulse lengths  $l_1 (=v \cdot t_1)$  and the lengths of the diffusion barriers  $X_D$ 's are greater than the diameters of the reaction tubes, which situation can be considered as a criterion for the one-dimensional approach. In the analysis above, abrupt edges of the reactive vapour pulses were assumed at the injection point. According to the source means of Fig. 5 this is easily achieved with standard valves. In the case of source means according to Figs. 6 and 7 a detailed analysis is necessary to ensure the intended situation. A lock condition of the source is achieved when diffusion barriers are formed in the tubes 43 and 12. Conditions for such diffusion barriers can be derived for the flow levels  $f_2$  and  $f_3$  in those tubes by differentiating equation (8), which gives the velocity  $v_d$  of an isobar in the gas phase medium

$$v_d = \frac{dx}{dt} = C_1 \sqrt{D}/\sqrt{t} = 2 C_1^2 D/x = 2 C_1^2 D^*/xp \quad (20)$$

A diffusion barrier is built up by a flow level,  $f_d$ , which gives a velocity  $v_1 - v_d$  of the gas phase medium in a channel with a sectional area  $A_1$

$$v_1 = f_d/A_1 \cdot p \quad 2C_1^2 D^*/xp \quad (21)$$

Then

$$f_d \geq 2A_1 C_1^2 D^*/x \quad (22)$$

In the flow circuit analogy of Fig. 7, the diffusion barrier conditions in channels 43 and 12 can be given by

$$f_{d2} \geq 2A_2 C_1^2 D^2 / L_2 \quad (23)$$

and

$$f_{d3} \geq 2A_3 C_1^2 D^2 / L_3 \quad (24)$$

where  $A_2$  and  $A_3$  are the sectional areas and  $L_2$  and  $L_3$  the lengths of the channels 43 and 12 respectively.

The pulse injection condition is obtained by letting a gas phase medium flow through the valve  $s_1$ . The rise time of the source injection is easily minimized in comparison to  $t_b$  and  $t_1$ , but certain attention must be paid to the values of source volume  $C$  and the conductance  $g_1$ ,  $g_2$  and  $g_3$ , in order to ensure a short delay at the switch off point. In general terms, a gas flow level  $f$ , through a channel, can be expressed in the form

$$f = g (p_a^2 - p_b^2) \quad (25)$$

where  $p_a$  and  $p_b$  are the pressures at the end of the channel, and  $g$  is a constant depending on the geometry of the channel and the properties of the gas in question. With the aid of equation (25) and the circuit analogy of Fig. 7, a solution is obtained to the source pressure  $p_o$  as a function of time from the switch off point of  $S_1$ , wherein

$$p_o = \frac{a \cdot e^{\tau t} + 1}{a \cdot e^{\tau t} - 1} \cdot p_{o\infty} \quad (26)$$

where  $p_{o\infty}$  is the source pressure at  $t=0$  and

$$a = (1 + p_{o\infty}/p_{co}) / (1 - p_{o\infty}/p_{co}) \quad (27)$$

$$p_{o\infty} = \sqrt{(g^x p_{r2}^2 + g_1 p_1^2) / (g^x + g_1)} \quad (28)$$

$$\tau = C / 2g^x p_{o\infty} \quad (29)$$

$$g^x = g_2 / (1 + g_2/g_3) \quad (30)$$

and

$$p^x = \sqrt{p_r^2 + f_o/g_3} \quad (31)$$

The pressure  $p_2$  (Fig. 7) has a value

$$p_2^2 = (f_o + g_2 p_o^2 + g_3 p_r^2) / (g_2 + g_3) \quad (32)$$

A diffusion barrier in 43 is obtained by setting  $f_2 = f_{d2}$

$$f_2 = g_2 (p_2^2 - p_o^2) \quad (33)$$

$$= g_2 (f_o + g_3 (p_r^2 - p_o^2) / (g_2 + g_3)) \geq f_{d2} \quad (34)$$

The build-up time  $t_b$  of the diffusion barrier, which is equal to the source pulse delay can be solved from (34) and (26), which give

$$t_b \geq \frac{1}{a} \ln \left( \frac{b+1}{b-1} \right) \quad (35)$$

where

$$b = \sqrt{(f_o + g_3 p_r^2 - f_{d2} (g_2 + g_3) / g_2) / g_3 / p_{o\infty}} \quad (36)$$

A safety limit to the minimum time interval  $t_1$  between two reactive pulses can be achieved by adding the pulse delay  $t_b$  to the time  $t_b$ .

The analysis made for the conditions of diffusion barriers in a gas phase medium were utilized for the embodiments of Figs. 2 and 3 and Figs. 10 and 11. The analysis is also directly applicable to the case of Figs. 8 and 9 and easily modified to the case of Figs. 13 and 14.

#### Examples

The following examples are given to further illustrate the present invention.

#### Example 1

The choices of structural and operational parameters for an embodiment of Figs. 10 and 11 are as follows:

Reaction zone:

length,  $L=40$  cm;

sectional area of the body,  $A_R=14 \times 14$  cm<sup>2</sup>;

free sectional flow area,  $A=150$  cm<sup>2</sup>;

exhaust pump speed,  $S=60$  m<sup>3</sup>/h.

Source means, Fig. 12:

source volume (41+42),  $C=210$  cm<sup>3</sup>;

source opening (43),  $\phi=0.7 \times 10$  cm;

$g_2=1400$  cm<sup>3</sup>/mbs;

source connection (12),  $\phi=1.1 \times 10$  cm;

$g_3=8800$  cm<sup>3</sup>/mbs;

exhaust connection (46),  $g_1=100$  cm<sup>3</sup>/mbs.

Operational parameters (typically)

reaction zone pressure,  $p_r=2$  mb;

source exhaust pump pressure,  $p_b=0.4$  mb;

gas phase medium (argon) flow/source,

$f_o=5500$  mbcms/s;

pulse pressure in source,  $p_{o\infty}=3$  mb.

Using the given parameters the following values can be calculated.

Equation (30):  $g^x=1208$  cm<sup>3</sup>/mbs;

Equation (28):  $p_{o\infty}=2.07$  mb;

Equation (36):  $b=1.067$ ;

Equation (22):  $f_{d2}=89$  mbcms/s corresponding to ppm isobar,  $p_1/p_o=10^{-8}$  in the center of the diffusion barrier;

Equation (29):  $\tau=0.030$  s;

Equation (35):  $t_b=0.05$  s;

Equation (14):  $t_b=0.74$  s.

A safety time interval between pulses is thus about  $t_1=0.8$  s. In practice a value  $t_1=1$  s has been used.

#### Example 2

Preparation of a Ta<sub>2</sub>O<sub>5</sub> compound thin film according to the parameters defined by example 1.

Substrates:

6 pieces  $0.3 \times 10 \times 20$  cm float glasses.

Temperature of the reaction zone  $T_R=300^\circ\text{C}$ .

#### Vapour substances:

Ta<sub>2</sub>Cl<sub>5</sub> from source, Fig. 12, at a temperature of 140°C, t<sub>1</sub>(Ta<sub>2</sub>Cl<sub>5</sub>)=0.2 s;

H<sub>2</sub>O from source means of Fig. 5, t<sub>1</sub>(H<sub>2</sub>O)=0.2 s, T(H<sub>2</sub>O)=15°C.

A growth of 2500 cycles gives a Ta<sub>2</sub>O<sub>5</sub> thin film of 1000Å on the substrates.

#### Example 2

Preparation of ZnS thin films doped with manganese, Mn.

Embodiment according to example 1.

Substrates as in example 2 or preferably Corning Glass 7059 (Tradename of Corning Glass Works, Corning, N.Y., U.S.A.).

Reactive zone temperature 450°C.

#### Reactive vapour substances:

ZnCl<sub>2</sub> and MnCl<sub>2</sub> from sources of Fig. 12 at 380°C and 510°C respectively. Source pulses of ZnCl<sub>2</sub> and MnCl<sub>2</sub> are given simultaneously with t<sub>1</sub>=0.2 s. Sulfidating agent H<sub>2</sub>S is given from source means of Fig. 5, t<sub>1</sub>(H<sub>2</sub>S)=0.2 s.

A growth of 4500 cycles gives a ZnS (Mn) film of 4000Å on the substrates.

#### Example 4

Thin films of



are prepared, according to examples 2 and 3, on glass substrates covered by a thin film of conducting transparent indium-tin-oxide, and the thin film is covered with a contact electrode of aluminum to provide an electroluminescence structure as illustrated in Fig. 15. In Fig. 15, the substrate 11 is covered with a transparent conducting layer of indium-tin-oxide 101, which in turn is covered by a first insulating film 102 of Ta<sub>2</sub>O<sub>5</sub>, a ZnS(Mn) film 103, a second insulating film 104 of Ta<sub>2</sub>O<sub>5</sub>, and an aluminum electrode 105 which enables application of an electric field across the sandwich structure between 101 and 105. With a sine wave excitation of 2 kHz, the brightness and efficiency characteristics of the structure are illustrated in Fig. 16. The curve B indicates the brightness in cd/m<sup>2</sup> against the excitation voltage, and the Curve C the efficiency of light output in lm/W.

#### Example 5

Preparation of an Al<sub>2</sub>O<sub>3</sub> thin film. The process used is similar to that of the example 2, with the Ta<sub>2</sub>Cl<sub>5</sub> replaced by AlCl<sub>3</sub> at a temperature of 95°C. A process of 2800 cycles gives a Al<sub>2</sub>O<sub>3</sub> thin film of thickness 2200 Å at the reaction zone temperature of 250°C. The electrical characteristics of the aluminum oxide film obtained was measured in a sandwich structure where the Al<sub>2</sub>O<sub>3</sub> film forms an insulator of a plate capacitor between aluminum thin film electrodes, with an active area of 5×5 mm. In Fig. 17 the curve C is the measured capacitance in pF as a function of frequency, and the curve tan ζ indicates the dielectric losses.

#### Claims

1. A method of performing an atomic layer epitaxy growth by growing a thin film of a compound of different elements on a substrate surface by providing alternate surface reactions of different substances containing said elements, comprising the steps of supplying vapours of said substances repeatedly and alternatively to a chamber housing said substrate, supplying a gas phase medium to said chamber at least during periods between the alternate supply of said substances, wherein said vapours react with the surfaces of the substrate and the film grown thereon to provide a solid state product at the temperature of said substrate surface, and wherein the supply of said gas phase medium substantially prevents a simultaneous interaction of said alternately supplied vapours during the growing of said thin film of said compound on said substrate.

2. A method as set forth in claim 1, wherein one of said alternate reactions is provided by supplying simultaneously first and second vapours which both react with said surfaces.

3. A method as set forth in claims 1 or 2, wherein said gas phase medium is supplied continuously.

4. A method as set forth in claim 1, wherein said step of supplying said gas phase medium is performed to carry residual vapour products from the chamber to an exhaust condensation zone, and to provide a diffusion barrier between the chamber and the exhaust condensation zone to prevent the flow of vapours from the condensation zone to the chamber.

5. A method as set forth in claim 1, wherein said vapours are supplied from vapour source outputs coupled to the chamber, and wherein said step of supplying a gas phase medium is performed to selectively and alternately provide diffusion barriers at said vapour source outputs.

6. An apparatus for carrying out the method as set forth in claims 1 to 5, comprising a chamber (18) for receiving a substrate (11); a suction pump (17) coupled to said chamber (18); heating means (15) for heating said substrate (11) within said chamber (18); a plurality of vapour sources (20, 41) coupled to said chamber (18) for selectively and separately supplying vapours of different substances from said vapour sources to said chamber (18); and a gas source (49) supplying a gas phase medium and being coupled to said chamber (18), and control means (44, S1) for controlling a flow of said gas phase medium through said chamber (18) from said gas source (49) to said suction pump means (17), said suction pump (17) being connected, with reference to the direction of flow (v) of said gas phase medium, to the output side of said chamber (18), said vapour sources (20, 41) being connected to the input side of said chamber (18), said gas source (49) being connected to a connecting tube (12, 43) between said vapour sources (20, 41) and said chamber (18), and said vapour sources (20, 41) at their side



opposite to said connecting tube (12, 43) being connected to a suction pump (50), whereby diffusion barriers are formed in said connecting tube (12, 43).

7. An apparatus as set forth in claim 6, characterized in that said gas source is connected by mediation of a pulse valve (44, S1) to said vapour sources (20, 41) on their side opposite to said connecting tube (12, 43) leading to said chamber (18).

8. An apparatus for carrying out the method as set forth in claims 1 to 5, comprising a chamber (18) for receiving a substrate (11); a suction pump (17) coupled to said chamber (18); heating means (15) for heating said substrate (11) within said chamber (18); a plurality of vapour sources (20, 41) coupled to said chamber (18) for selectively and separately supplying vapours of different substances from said vapour sources to said chamber; a gas source (28) supplying a gas phase medium and being coupled to said chamber (18); and control means for controlling a flow of said gas phase medium through said chamber (18) from said gas source (28) to said suction pump means (17), said suction pump (17) being connected, with reference to the direction of flow (v) of said gas phase medium, to the output side of said chamber (18), said vapour sources (20, 41) being connected to the input side of said chamber (18), said gas source (28) being connected to a connecting tube (12, 25) between said vapour sources (20, 41) and said chamber (18), a mechanical valve means (21, 22, 23, 26) being provided with reference to the direction of flow of said vapours, upstream of the connection between said connecting tube (12, 25) and said gas source (28).

9. An apparatus for carrying out the method as set forth in claims 1 to 5, comprising a chamber for receiving a substrate (11'); a suction pump coupled to said chamber; heating means (68) for heating said substrate (11') within said chamber; a plurality of vapour sources (53, 54) coupled to said chamber for selectively and separately supplying vapours of different substances from said vapour sources to said chamber and a gas source (66, 67) supplying a gas phase medium and being coupled to said chamber; control means for controlling a flow of said gas phase medium through said chamber from said gas source to said suction pump means, said suction pump being connected, with reference to the direction of flow of said gas phase medium, to the output side of said chamber and said vapour sources (53, 54) and said gas source (66, 67) being connected to the input side of said chamber, and a rotatably moveable substrate holder (61) provided within said chamber, so that a given point of said substrate will pass alternately through a gas phase medium region and through regions containing said vapours of said different substances, said moveable substrate holder (61) consisting of a member resembling a paddle wheel rotatable about an axis and disposed between sections of the apparatus body (60) said

sections each in their turn constituting flow passages (55, 55') for said gas phase medium, connected by one end to said suction pump and by their other end to said gas source (66, 67), and flow passages (51, 51', 52, 52') for said different vapours connected by one end to said suction pump and by their other end to said vapour sources (53, 54).

10. An apparatus for carrying out the method as set forth in claim 1 to 5, comprising a chamber for receiving a substrate (11'); a suction pump coupled to said chamber; heating means for heating said substrate (11') within said chamber; a plurality of vapour sources (81, 82) coupled to said chamber for selectively and separately supplying vapours of different substances from said vapour sources to said chamber; and a gas source (77) supplying a gas phase medium and being coupled to said chamber; control means for controlling a flow of said gas phase medium through said chamber from said gas source to said suction pump means, a rectilinearly moveable substrate holder for said substrate, and a distribution member (72) for said gas phase medium and for said vapours of said substances, which member (72) comprises alternate gas or vapour feed openings (73, 75), respectively connected to said gas source and vapour sources, and exhaust openings (74) coupled to said suction pump, said substrate (11') being disposed adjacent to said openings in such a way that on being caused to move a given point of said substrate will pass alternately through the diffusion wall constituted by the flow of said gas phase medium and through said vapours.

#### Revendications

1. Procédé de mise en oeuvre de croissance d'une couche atomique par épitaxie en faisant croître une fine pellicule d'un composé de différents éléments sur la surface d'un substrat en réalisant des réactions de surface alternées de différentes substances contenant lesdits éléments, comprenant les étapes de fourniture des vapeurs desdites substances de façon répétée et alternée dans une chambre abritant ledit substrat, de fourniture d'un milieu à phase gazeuse dans ladite chambre au moins pendant les périodes entre la fourniture alternée desdites substances, dans lequel lesdites vapeurs réagissent avec les surfaces du substrat et la pellicule formée dessus pour fournir un produit à l'état solide à la température de ladite surface du substrat, et dans lequel la fourniture dudit milieu à phase gazeuse évite sensiblement une interaction simultanée desdites vapeurs admises alternativement pendant la croissance de ladite fine pellicule dudit composé sur ledit substrat.

2. Procédé comme exposé dans la revendication 1, dans lequel l'une desdites réactions alternées est obtenue en fournissant simultanément les premières et secondes vapeurs qui réagissent toutes deux avec lesdites surfaces.

3. Procédé comme décrit dans les reven-

dications 1 ou 2, dans lequel ledit milieu à phase gazeuse est fourni de façon continue.

4. Procédé comme décrit dans la revendication 1, dans lequel ladite étape de fourniture dudit milieu à phase gazeuse est réalisée pour véhiculer les produits résiduels à l'état de vapeur de la chambre jusqu'à une zone de condensation et d'évacuation, et pour fournir une barrière de diffusion entre la chambre et la zone de condensation et d'évacuation pour empêcher la circulation des vapeurs de la zone de condensation à la chambre.

5. Procédé comme décrit dans la revendication 1, dans lequel lesdites vapeurs sont fournies à partir de sorties de source de vapeurs accouplées à la chambre, et dans lequel ladite étape de fourniture d'un milieu à phase gazeuse est réalisé pour fournir sélectivement et alternativement des barrières de diffusion auxdites sorties de sources de vapeurs.

6. Appareil pour réaliser le procédé comme décrit dans les revendications 1 à 5, comprenant une chambre (18) pour recevoir un substrat (11); une pompe aspirante (17) couplée à ladite chambre (18); des moyens de chauffage (15) pour chauffer ledit substrat (11) à l'intérieur de ladite chambre (18); une pluralité de sources de vapeurs (20, 41) couplées à ladite chambre (18) pour fournir sélectivement et séparément des vapeurs de différentes substances provenant desdites sources de vapeur à ladite chambre (18); et une source de gaz (49) fournissant un milieu à phase gazeuse et qui est couplée à ladite chambre (18); et des moyens de réglage (44, 51) pour régler un courant dudit milieu à phase gazeuse à travers ladite chambre (18) à partir de ladite source de gaz (49) auxdits moyens de pompe aspirante (17) ladite pompe aspirante (17) étant reliée, par rapport à la direction du courant (v) dudit milieu à phase gazeuse, au côté de sortie de ladite chambre (18), lesdites sources de vapeurs (20, 41) étant reliées au côté d'entrée de ladite chambre (18), ladite source de gaz (49) étant reliée à une tube de jonction (12, 43) entre lesdites sources de vapeur (20, 41) et ladite chambre (18) et lesdites sources de vapeur (20, 41) étant reliées, sur leur côté opposé audit tube de connexion (12, 43), à une pompe aspirante (50), grâce à quoi des barrières de diffusion sont formées dans ledit tube de jonction (12, 43).

7. Appareil comme décrit dans la revendication 6, caractérisé en ce que ladite source de gaz est reliée par l'intermédiaire d'une soupape à impulsion (44, 51) auxdites sources de vapeur (20, 41) sur leur côté opposé audit tube de jonction (12, 43) conduisant à ladite chambre (18).

8. Appareil pour réaliser le procédé comme décrit dans les revendications 1 à 5 comprenant une chambre (18) pour recevoir un substrat (11); une pompe aspirante (17) couplée à ladite chambre (18); des moyens de chauffage (15) pour chauffer ledit substrat (11) à l'intérieur de ladite chambre (18); une pluralité de sources de vapeurs (20, 41) couplées à ladite chambre (18) la fourniture sélectivement et séparément des

vapeurs de différentes substances provenant desdites sources de vapeurs à ladite chambre; une source de gaz (28) fournissant un milieu à phase gazeuse et qui est couplé à ladite chambre (18); et des moyens de réglage pour régler un courant dudit milieu à phase gazeuse à travers ladite chambre (18) de ladite source de gaz (28) auxdits moyens de pompe aspirante (17), ladite pompe aspirante (17) étant reliée, par rapport à la direction du courant (v) dudit milieu à phase gazeuse, à la face de sortie de ladite chambre (18), lesdites sources de vapeurs (20, 41) étant reliées au côté d'entrée de ladite chambre (18), ladite source de gaz (28) étant reliée à une tube de jonction (12, 25) entre lesdites sources de vapeurs (20, 41) et ladite chambre (18), des moyens de soupape mécanique (21, 22, 23, 26) étant prévue par rapport à la direction du courant desdites vapeurs, en amont de la jonction entre ledit tube de jonction (12, 25) et ladite source de gaz (28).

9. Appareil pour réaliser le procédé comme décrit dans les revendications 1 à 5, comprenant une chambre pour recevoir un substrat (11'); une pompe aspirante couplée à ladite chambre; des moyens de chauffage (68) pour chauffer ledit substrat (11') à l'intérieur de ladite chambre; une pluralité de sources de vapeurs (53, 54) couplées à ladite chambre pour fournir sélectivement et séparément des vapeurs de différentes substances provenant desdites sources de vapeurs à ladite chambre; et une source de gaz (66, 67) fournissant un milieu à phase gazeuse et qui est couplée à ladite chambre; des moyens de réglage pour régler un courant dudit milieu à phase gazeuse à travers ladite chambre de ladite source de gaz audit moyen de pompe aspirante, ladite pompe aspirante étant reliée, par rapport à la direction du courant dudit milieu à phase gazeuse, au côté de sortie de ladite chambre et lesdites sources de vapeurs (53, 54) et ladite source de gaz (66, 67) étant reliées au côté d'entrée de ladite chambre, et un support de substrat susceptible de se déplacer en tournant (61) prévu à l'intérieur de ladite chambre, de sorte qu'un point donné dudit substrat passera alternativement à travers une zone du milieu à phase gazeuse et à travers des zones contenant lesdites vapeurs desdites différentes substances, ledit support de substrat mobile (61) comprenant une partie ressemblant à une roue à palettes susceptible de tourner autour d'une axe et disposé entre des sections du corps de l'appareil (60), lesdites sections constituant chacune à leur tour des passages de courant (55, 55') pour ledit milieu à phase gazeuse, reliés à une extrémité à ladite pompe aspirante et à l'autre extrémité à ladite source de gaz (66, 67), et des passages de courant (51, 51', 52, 52') pour lesdites différentes vapeurs reliés par une extrémité à ladite pompe aspirante et par l'autre extrémité auxdites sources de vapeur (53, 54).

10. Appareil pour réaliser le procédé comme décrit dans les revendications 1 à 5, comprenant une chambre pour recevoir un substrat (11'); une pompe aspirante couplée à ladite chambre; des

moyens de chauffage pour chauffer ledit substrat (11') à l'intérieur de ladite chambre; une pluralité de sources de vapeurs (81, 82) couplées à ladite chambre pour admettre sélectivement et séparément des vapeurs de différentes substances desdites sources de vapeurs à ladite chambre; et une source de gaz (77) fournissant un milieu à phase gazeuse et qui est couplée à ladite chambre; des moyens de contrôle pour régler un courant dudit milieu à phase gazeuse à travers ladite chambre de ladite source de gaz auxdits moyens de pompe aspirante, un support de substrat déplaçable linéairement pour ledit substrat, et un organe de distribution (72) pour ledit milieu à phase gazeuse et pour lesdites vapeurs desdites substances, lequel organe (72) comprend des ouvertures alternées d'alimentation en gaz ou en vapeurs (73), reliées respectivement à ladite source de gaz et auxdites sources de vapeurs, et des ouvertures de sorties (74) reliées à ladite pompe aspirante, ledit substrat (11') étant disposé de façon adjacente auxdites ouvertures de telle manière que lorsqu'il est amené à bouger un point donné dudit substrat passe alternativement à travers la paroi de diffusion constituée par le courant dudit milieu à phase gazeuse et à travers lesdites vapeurs.

#### Patentansprüche

1. Verfahren zum Bewirken eines Atomschichtepitaxie-Aufwachsens durch Aufwachsenlassen einer aus einer Verbindung verschiedener Elemente bestehenden Dünnschicht auf eine Substratoberfläche, indem abwechselnde Oberflächenreaktionen verschiedener Substanzen, die die Elemente enthalten, herbeigeführt werden, mit den Schritten der wiederholten und abwechselnden Zuführung von Dämpfen der Substanzen zu einer das Substrat aufnehmenden Kammer und der mindestens während Zeitabschnitten zwischen der abwechselnden Zuführung der Substanzen erfolgenden Zuführung eines gasförmigen Mediums zu der Kammer, wobei die Dämpfe unter Bildung eines im festen Zustand befindlichen Produkts bei der Temperatur der Substratoberfläche mit den Oberflächen des Substrats und der darauf aufgewachsenen Dünnschicht reagieren und wobei die Zuführung des gasförmigen Mediums eine gleichzeitige Wechselwirkung der abwechselnd zugeführten Dämpfe während des Aufwachsens der aus der Verbindung bestehenden Dünnschicht auf das Substrat im wesentlichen verhindert.

2. Verfahren nach Anspruch 1, bei dem eine der abwechselnden Reaktionen dadurch herbeigeführt wird, daß gleichzeitig ein erster und ein zweiter Dampf, die beide mit den Oberflächen reagieren, zugeführt werden.

3. Verfahren nach Anspruch 1 oder 2, bei dem das gasförmige Medium kontinuierlich zugeführt wird.

4. Verfahren nach Anspruch 1, bei dem der Schritt der Zuführung des gasförmigen Mediums

durchgeführt wird, um restliche dampfförmige Produkte aus der Kammer zu einer Kondensationszone für ausströmende Dämpfe zu tragen und um zwischen der Kammer und der Kondensationszone für ausströmende Dämpfe eine Diffusionssperre zur Verhinderung des Ausströmens von Dämpfen aus der Kondensationszone zu der Kammer zu bilden.

5. Verfahren nach Anspruch 1, bei dem die Dämpfe aus Dampfquellenausgängen, die mit der Kammer verbunden sind, zugeführt werden und bei dem der Schritt der Zuführung eines gasförmigen Mediums durchgeführt wird, um an den Dampfquellenausgängen selektiv und abwechselnd Diffusionssperren zu bilden.

6. Vorrichtung zur Durchführung des Verfahrens nach Ansprüchen 1 bis 5 mit einer Kammer (18) für die Aufnahme eines Substrats (11); einer mit der Kammer (18) verbundenen Saugpumpe (17); einer Heizeinrichtung (15) zum Erwärmen des Substrats (11) innerhalb der Kammer (18); mehr als einer mit der Kammer (18) verbundenen Dampfquelle (20, 41) für die selektive und getrennte Zuführung von Dämpfen verschiedener Substanzen aus den Dampfquellen zu der Kammer (18); einer Gasquelle (49), die ein gasförmiges Medium zuführt und mit der Kammer (18) verbunden ist; und einer Steuereinrichtung (44, S<sub>1</sub>) zum Steuern eines Stromes des gasförmigen Mediums durch die Kammer (18) von der Gasquelle (49) zu der Saugpumpeneinrichtung (17), wobei die Saugpumpe (17) mit der Ausgangsseite der Kammer (18) in bezug auf die Strömungsrichtung (v) des gasförmigen Mediums verbunden ist, die Dampfquellen (20, 41) mit der Eingangsseite der Kammer (18) verbunden sind, die Gasquelle (49) mit einem Verbindungsrohr (12, 43) zwischen den Dampfquellen (20, 41) und der Kammer (18) verbunden ist und die Dampfquellen (20, 41) an ihrer dem Verbindungsrohr (12, 43) entgegengesetzten Seite mit einer Saugpumpe (50) verbunden sind, wodurch in dem Verbindungsrohr (12, 43) Diffusionssperren gebildet werden.

7. Vorrichtung nach Anspruch 6, dadurch gekennzeichnet, daß die Gasquelle durch Vermittlung eines Impulsventils (44, S<sub>1</sub>) mit den Dampfquellen (20, 41) an deren dem Verbindungsrohr (12, 43), das zu der Kammer (18) führt, entgegengesetzter Seite verbunden ist.

8. Vorrichtung zur Durchführung des Verfahrens nach Ansprüchen 1 bis 5 mit einer Kammer (18) für die Aufnahme eines Substrats (11); einer mit der Kammer (18) verbundenen Saugpumpe (17); einer Heizeinrichtung (15) zum Erwärmen des Substrats (11) innerhalb der Kammer (18); mehr als einer mit der Kammer (18) verbundenen Dampfquelle (20, 41) für die selektive und getrennte Zuführung von Dämpfen verschiedener Substanzen aus den Dampfquellen zu der Kammer; einer Gasquelle (28), die ein gasförmiges Medium zuführt und mit der Kammer (18) verbunden ist; und einer Steuereinrichtung zum Steuern eines Stromes des gasförmigen Mediums durch die Kammer (18) von der Gas-

quelle (28) zu der Saugpumpeneinrichtung (17), wobei die Saugpumpe (17) mit der Ausgangsseite der Kammer (18) in bezug auf die Strömungsrichtung (v) des gasförmigen Mediums verbunden ist, die Dampfquellen (20, 41) mit der Eingangsseite der Kammer (18) verbunden sind und die Gasquelle (28) mit einem Verbindungsrohr (12, 25) zwischen den Dampfquellen (20, 41) und der Kammer (18) verbunden ist und wobei stromaufwärts von der Verbindung zwischen dem Verbindungsrohr (12, 25) und der Gasquelle (28) in bezug auf die Strömungsrichtung der Dämpfe eine mechanische Ventileinrichtung (21, 22, 23, 26) vorgesehen ist.

9. Vorrichtung zur Durchführung des Verfahrens nach Ansprüchen 1 bis 5 mit einer Kammer für die Aufnahme eines Substrats (11'); einer mit der Kammer verbundenen Saugpumpe; einer Heizeinrichtung (68) zum Erwärmen des Substrats (11') innerhalb der Kammer; mehr als einer mit der Kammer verbundenen Dampfquelle (53, 54) für die selektive und getrennte Zuführung von Dämpfen verschiedener Substanzen aus den Dampfquellen zu der Kammer; einer Gasquelle (66, 67), die ein gasförmiges Medium zuführt und mit der Kammer verbunden ist; einer Steuereinrichtung zum Steuern eines Stromes des gasförmigen Mediums durch die Kammer von der Gasquelle zur der Saugpumpeneinrichtung, wobei die Saugpumpe mit der Ausgangsseite der Kammer in bezug auf die Strömungsrichtung des gasförmigen Mediums verbunden ist und die Dampfquellen (53, 54) und die Gasquelle (66, 67) mit der Eingangsseite der Kammer verbunden sind, und einem drehbar, beweglichen Substrathalter (61), der innerhalb der Kammer vorgesehen ist, so daß eine bestimmte Stelle des Substrats abwechselnd durch einen Bereich des gasförmigen Mediums und durch Bereiche, die die Dämpfe der verschiedenen Substanzen enthalten, hindurchgeht, wobei der bewegliche Substrathalter (61) aus einem Bauteil besteht, das einem

Schaufelrad ähnelt, um eine Achse herum drehbar ist und zwischen Abschnitten des Vorrichtungskörpers (60) angeordnet ist, wobei die Abschnitte nacheinander Strömungsdurchgänge (55, 55') für das gasförmige Medium, die an einem Ende mit der Saugpumpe und an ihren anderen Ende mit der Gasquelle (66, 67) verbunden sind, und Strömungsdurchgänge (51, 51', 52, 52') für die verschiedenen Dämpfe, die an einem Ende mit der Saugpumpe und an ihren anderen Ende mit den Dampfquellen (53, 54) verbunden sind, bilden.

10. Vorrichtung zur Durchführung des Verfahrens nach Ansprüchen 1 bis 5 mit einer Kammer für die Aufnahme eines Substrats (11'); einer mit der Kammer verbundenen Saugpumpe; einer Heizeinrichtung zum Erwärmen des Substrats (11') innerhalb der Kammer; mehr als einer mit der Kammer verbundenen Dampfquelle (81, 82) für die selektive und getrennte Zuführung von Dämpfen verschiedener Substanzen aus den Dampfquellen zu der Kammer; einer Gasquelle (77), die ein gasförmiges Medium zuführt und mit der Kammer verbunden ist; einer Steuereinrichtung zum Steuern eines Stromes des gasförmigen Mediums durch die Kammer von der Gasquelle zu der Saugpumpeneinrichtung; einem geradlinig beweglichen Substrathalter für das Substrat und einem Verteilungs-Bauteil (72) für das gasförmige Medium und die Dämpfe der Substanzen, wobei das Bauteil (72) abwechselnde Gas- oder Dampfzuführungsöffnungen (73, 75), die mit der Gasquelle bzw. den Dampfquellen verbunden sind, und Auslaßöffnungen (74), die mit der Saugpumpe verbunden sind, aufweist, wobei das Substrat (11') derart an die Öffnungen angrenzend angeordnet ist, daß eine bestimmte Stelle des Substrats, wenn veranlaßt wird, daß sie sich bewegt, abwechselnd durch die Diffusionswand, die durch den Strom des gasförmigen Mediums gebildet wird, und durch die Dämpfe hindurchgeht.

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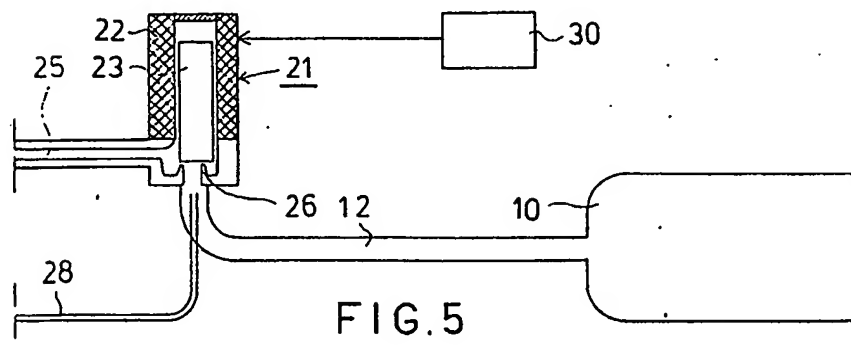
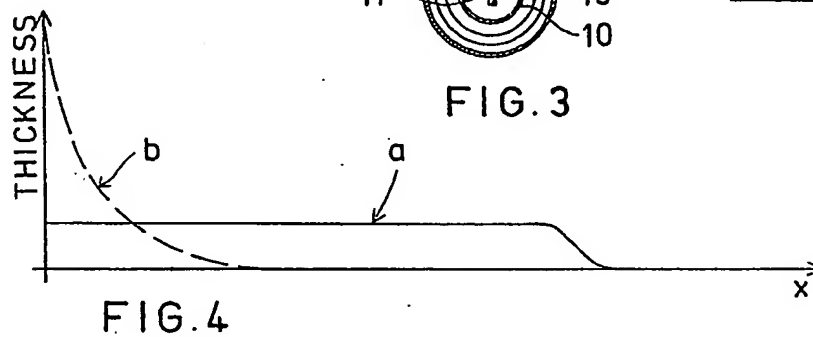
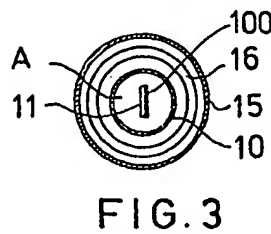
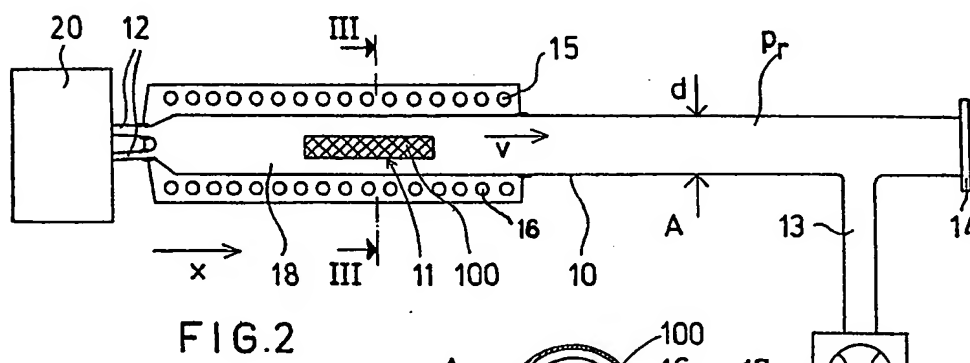
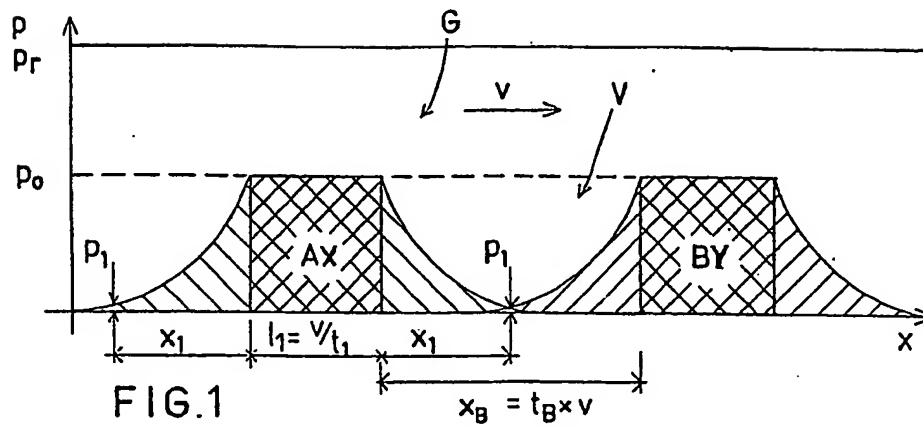
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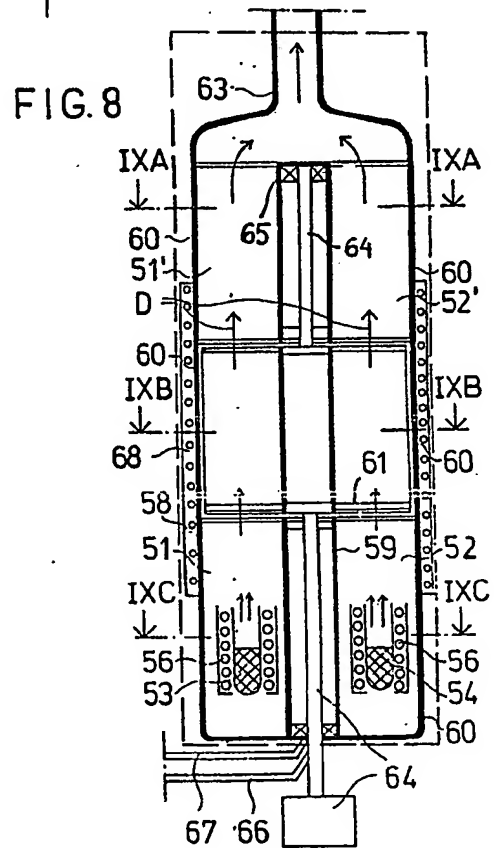
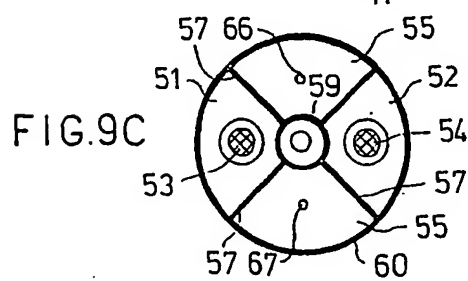
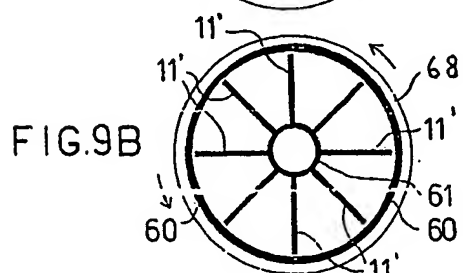
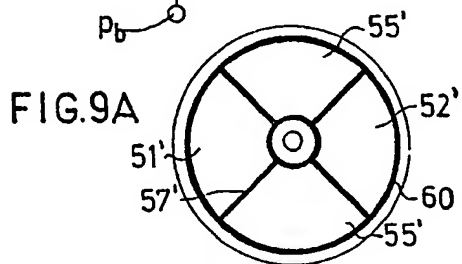
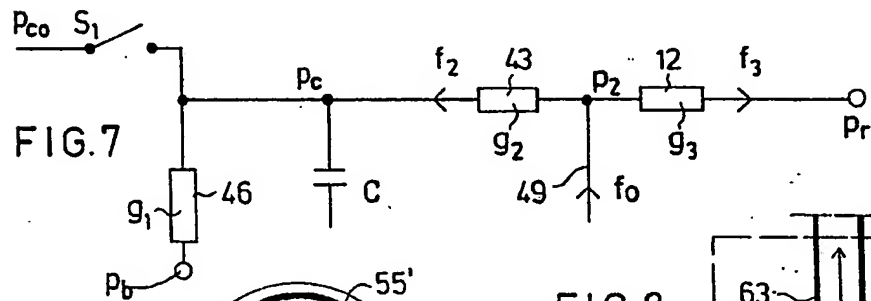
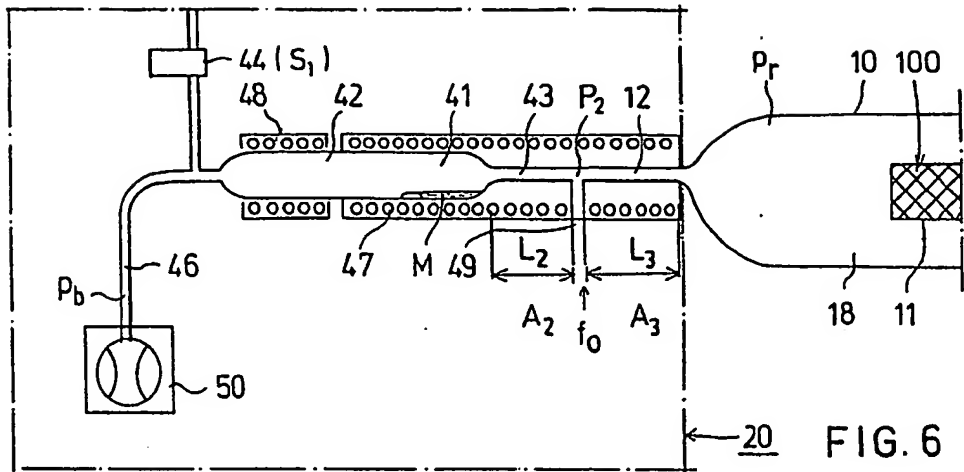
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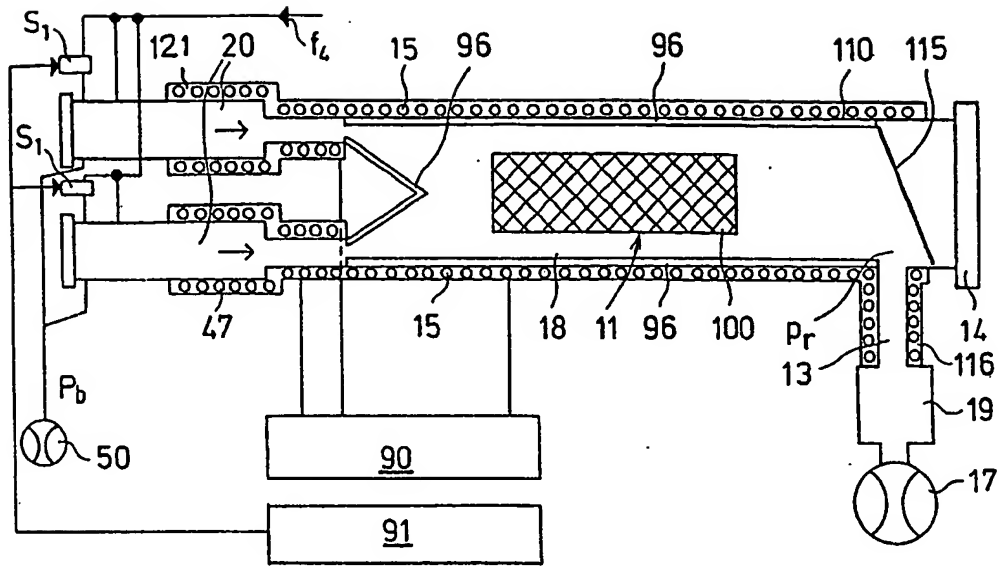


FIG. 10

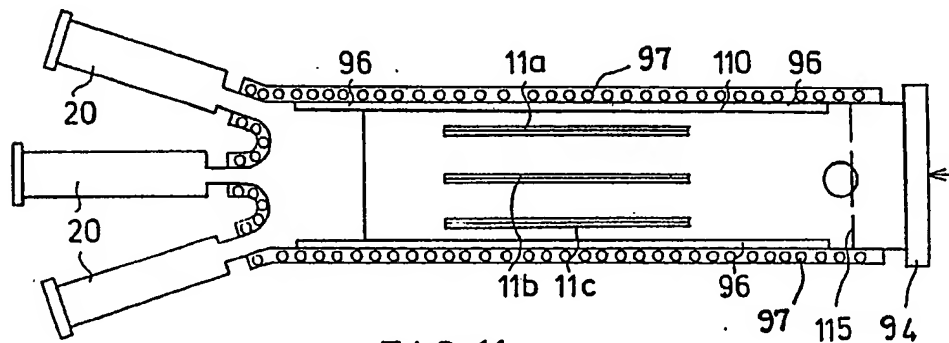


FIG. 11

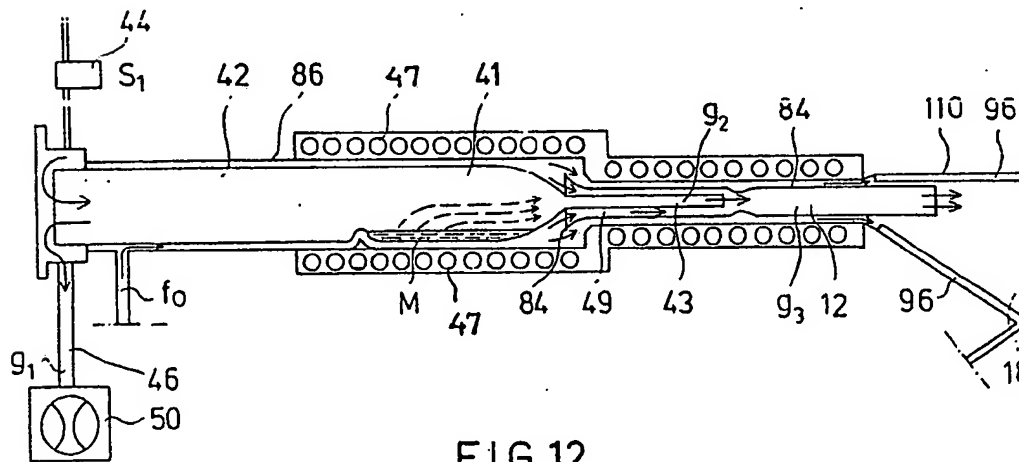


FIG. 12





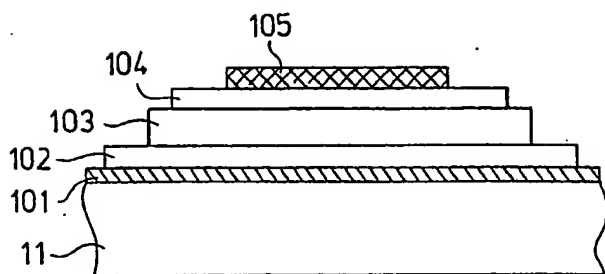


FIG. 15

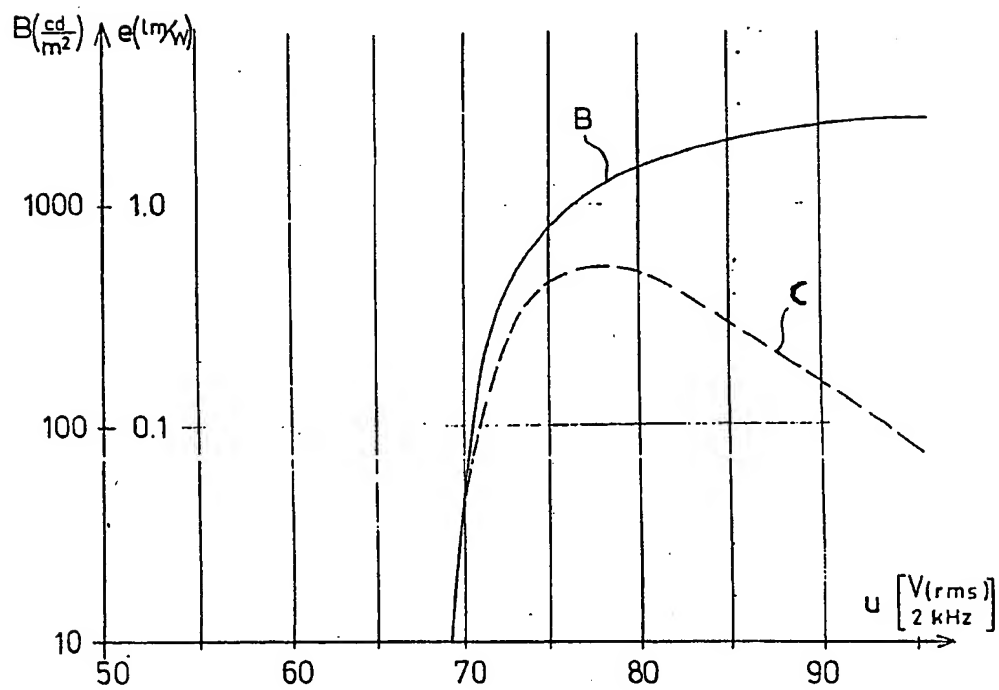


FIG. 16